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Radiothermoluminescence (RTL) involves irradiating a solid at low temperature (77K) with ionizing radiation and observing luminescence when heating the sample at a constant rate (10 K/min). Glow peaks are observed at characteristic temperatures which, for polymers, are diagnostic of the onset of thermally activated molecular motions. A scanning electron microscope (SEM) was modified to irradiate polymer samples with medium energy (5-30 keV) electrons. This SEM-RTL device is more convenient and reliable than other techniques which utilize remote radiation sources, though information is confined to the near surface regions of the sample. In particular, the oxygen-free environment of the SEM-RTL experiment permitted observation of high temperature relaxations (up to 150°C or 423 K) for the first time in a number of thermoplastics. Experiments on model ethylene copolymers suggest that absolute RTL intensities are not reliable; this makes uncertain the interpretation of relative intensities of RTL peaks in different polymers. RTL peaks are much narrower than mechanical or dielectric loss peaks for reasons which are not understood.

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RADIOTHERMOLUMINESCENCE STUDIES OF POLYMER SOLIDS

FINAL REPORT

BUCKLEY CRIST, JR.

APRIL 1, 1989

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NORTHWESTERN UNIVERSITY

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CONTENTS

I. INTRODUCTION

A. General Background

Polymers display a rich variety of molecular mobilities which are known (or at least suspected) to be related to macroscopic mechanical properties. These motions are thermally activated, with the correlation time τ being given by expressions of the form:

$$\tau = \tau_0 \exp [E_a/RT] \tag{1a}$$

$$\tau = \tau_0 \exp [B/(T-T_0)] \tag{1b}$$

Here τ_0 is a fundamental time period, typically on the order of $10^{-5} - 10^{-12}$ sec, which is indicative of the size of the moving entity within the macromolecule. Arrhenius behavior is accounted for by eqn. 1a, wherein E_a is the activation energy and thermal energy is represented by RT. Equation 1b is used to describe the important glass transition which is characterized by a high degree of cooperativity among the dynamic elements. Here the characteristic temperature T_0 is often observed to be about T_g-50 K, where T_g is the glass transition temperature.[1]

Molecular mobility in polymer solids is a mature subject of scientific and technological importance. A variety of experimental methods are available for studying such effects. Dynamic mechanical and dielectric relaxation are the two which are most commonly employed.[2] Nuclear magnetic relaxation, calorimetry and dilatometry are also conventional techniques.[3] Each of these tools has certain characteristics which render it more or less useful. All methods are capable of defining a "transition" temperature at which τ has a particular average value determined by the time scale or

frequency of the experiment. By measuring the dependence of τ on temperature the relevant parameters in eqn. 1a or 1b can be evaluated. More detailed information is in principle contained in the shape and intensity of the response function (e.g., the width and height of a relaxation peak). At this level of analysis both nuclear magnetic and dielectric relaxation are superior because various dynamic models can be used to simulate the experimental results. Dynamic mechanical relaxation generally suffers from the inability to interpret relaxation strengths.

It is fair to say that our understanding of dynamics in solid polymers is far from satisfactory - for instance, does a "glass transition" occur in the noncrystalline regions of a semicrystalline polymer? Nevertheless, there are many empirical correlations between relaxation spectra and various engineering properties of interest. These range from elastic modulus (which can be understood qualitatively in terms of compliance mechanisms activated by various motions) to fracture behavior. Some of these relations are covered in Chapter 4 of reference 3.

B. Research Objectives.

In the 1960's a new method for observing molecular motions in organic solids was developed; radiothermoluminescence (RTL) has been applied to polymers for over 25 years.[4] There are two general goals in this work: to devise an RTL experiment based on electron irradiation; to explore in a more quantitative sense some of the unique features of RTL spectra.

The vast majority of RTL experiments have employed γ-rays from a ^{60}Co source for irradiation. This practice is obviously inconvenient, as few researchers have access to suitable radiation facilities. Remote irradiation by whatever means inevitably leads to complications with sample handling and environment control during the subsequent heating step. In this research we have developed a simple modification to a scanning electron microscope (SEM) which permits rapid irradiation and subsequent heating under well controlled conditions. It is believed that this represents a significant advance, as RTL is shown to be feasible in almost any laboratory having a SEM.

Some of the fundamental aspects of the nature of RTL spectra, i.e., the shapes and intensities of the peaks, were considered. On a more phenomenological level, the RTL spectra of many polymers were surveyed for more qualitative information regarding molecular mobility.

C. Description of Radiothermoluminescence

A current review of RTL as applied to polymers is presented in a monograph[3] written by L. Zlatkevich, the Research Associate active in this project. An earlier overview was presented by Partridge.[5] Pertinent points for this work are summarized here.

The polymer solid is subjected to ionizing radiation (typically γ-rays, although X-rays, UV light or electrons may be employed) at a low temperature (usually 77 K). The sample is heated at a constant rate β [K/sec] while being observed by a photodetector. The resulting "glow curve" (see Fig. 1) is a series
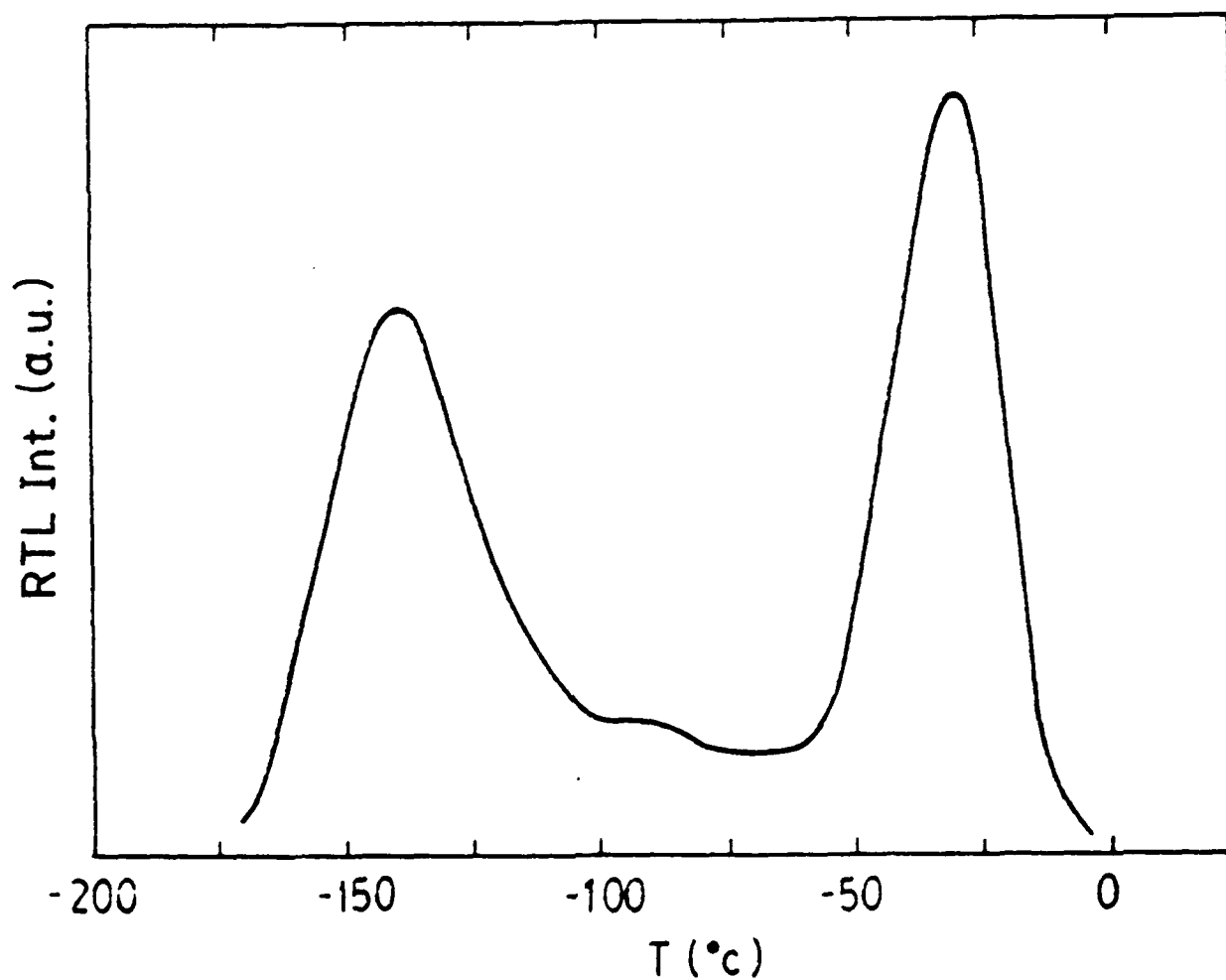
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Fig. 1 RTL glow curve for linear low density polyethylene. Two strong peaks are seen at -140°C and -30°C, and there is a weak maximum near -90°C. Spectrum obtained with conventional RTL procedure following γ-irradiation at 77 K (-196°C).

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of peaks centered at discrete temperatures where the luminescent flux from the irradiated polymer is maximized. In general terms, these RTL peaks occur because of recombination and/or deexitation of species formed by the low temperature radiation process. The following series of reactions is thought to be representative of the chemical and physical events which occur.[3,5]

$$M \xrightarrow{\text{rad}} M^+ + e_t^- \qquad (2)$$

$$M^+ + e_t^- \rightarrow M^* \qquad (3a)$$

$$M^* + L \rightarrow M + L^* \qquad (3b)$$

$$L^* \rightarrow L + h\upsilon \qquad (3c)$$

Equation 2 indicates that macrocations M^+ and trapped electrons e_t^- are formed and stabilized during low temperature irradiation. Equations 3a-3c indicate a series of reactions which first involve recombination of the charged species to form an excited neutral polymer M^* at some higher temperature. This is followed by energy transfer to a suitable luminescent impurity L (eqn. 3b) which subsequently decays to the ground state with emission of radiant energy $h\upsilon$ (eqn. 3c).

An important working hypothesis is that the initial charge recombination step, eqn. 3a, is the rate limiting reaction governing light emission. If one assumes first order kinetics:

$$\frac{d[n]}{dt} = -K[n] \qquad (4)$$

where [n] is the concentration of either charged species ($[M^+]$ or $[e_t^-]$, which should be equal), the observed light intensity I

obser ed during heating the sample at a rate ß, assuming Arrhenius thermal activation of the rate constant K, is

$$I(T,\beta) = \alpha[n_o]\omega \exp[-(E_a/RT)-(\omega/\beta)\int_{T_o}^{T}\exp(-E_a/RT)dT] \qquad (5)$$

Here $[n_o]$ is the original concentration of charged species formed by irradiation at temperature T_o, and α is the fraction of those which result in luminescence by eqn. 3. The kinetic parameters ω [sec^{-1}] and E_a [Joule/mole] are the frequency factor and activation energy respectively, for recombination:

$$K = \omega \exp[-E_a/RT] \qquad (6)$$

A luminescence peak such as in Fig. 1 can be understood as follows. The reaction rate becomes appreciable (on a time scale established by the heating rate ß) at some temperature greater than T_o. The rate initially increases with the temperature dependence of the rate constant K (eqn. 6). After some time a majority of the charges have recombined, and the rate slows as [n] approaches zero (eqn. 4.) The temperature of the intensity peaks, T_p, can be obtained by differentiation of eqn. 5 which gives

$$T_p^2 \exp[-E_a/RT_p] = E_a\beta/R\omega \qquad (7)$$

The activation energy E_a can be determined independently from the initial rise (low temperature tail) of a peak, permitting evaluation of ω. Alternatively, T_p can be measured at a series of heating rules ß to determine both E_a and ω.

For most polymers one sees multiple RTL peaks which frequently (though not always) correspond to the temperature ranges of thermally activated molecular motions. This implies that the kinetics of the recombination reaction, embodied in the absolute value and temperature dependence of the rate constant K (eqn. 6), reflect the dynamics of the polymer matrix in which the charges are trapped. There is much research on thermoluminescence from inorganic solids, in which the equivalent recombination kinetics are controlled by the depth of the energy trap which localizes one (or both) of the trapped charges. In polymers, however, the recombination rate is controlled by diffusion mechanisms which permit the trapped charges to approach one another. In other words, the activation energy E_a is appropriate for some sort of intra- or intermolecular mobility, and is not a function of the trapping energy. This point is discussed in some detail in Chapter 3 of reference 3.

Analysis of glow curves or RTL spectra of polymers is usually confined to peak positions and relative intensities of the various peaks. These can be changed by chemical composition (copolymers and blends) and by thermal and mechanical history. Reference 3 contains an extensive survey of RTL studies of glassy and semicrystalline polymers.

II. RESEARCH RESULTS

A. RTL Apparatus

Two RTL devices were used in this work. These are described below.

1. <u>Conventional RTL Apparatus</u>. This simple unit, which detects thermoluminescence in samples which have been irradiated by γ-rays from a ^{60}Co source, was supplied by Dr. Zlatkevich. As shown in Fig. 2, it consists of variable temperature sample chamber and a photomultiplier tube (PMT) detector.[6] The sample, in a ferrous metal curvette placed in a glass tube, is first outgassed ($P < 10^{-6}$ Torr) and then exposed to ca. 1 Mrad of γ-rays from a ^{60}Co source. For these experiments the source at Argonne National Laboratories was used.

Irradiation is done at liquid nitrogen temperature (77 K) and samples are stored away from light in liquid nitrogen until the RTL analysis is done. The conventional RTL device is first cooled to about 90 K (-183°C) by circulating liquid nitrogen. Transfer of the irradiated sample into the device is facilitated by the magnetic sample holder, but invariably some sample warming and exposure to light and oxygen occurs. After sample loading, heating is accomplished at a predetermined rate β (typically 10°/min or 0.16°/sec). Luminescence is recorded as a function of time (temperature); detection by the PMT is enhanced by the polished light guide.

2. <u>Scanning Electron Microscope - RTL (SEM-RTL)</u>. It was decided to use a "surplus" Cambridge S4 SEM to provide both the
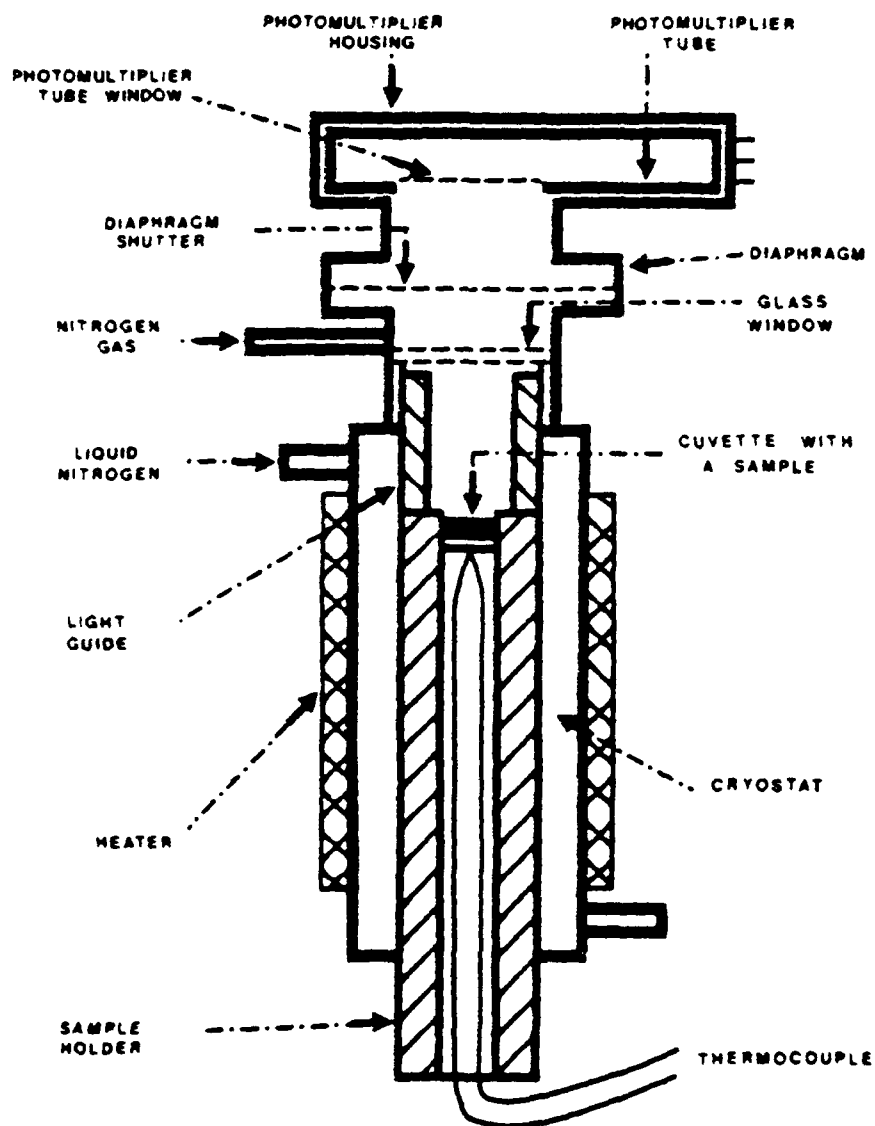
PHOTOMULTIPLIER TUBE WINDOW

PHOTOMULTIPLIER HOUSING

PHOTOMULTIPLIER TUBE

DIAPHRAGM SHUTTER

DIAPHRAGM

GLASS WINDOW

NITROGEN GAS

LIQUID NITROGEN

CUVETTE WITH A SAMPLE

LIGHT GUIDE

CRYOSTAT

HEATER

SAMPLE HOLDER

THERMOCOUPLE

Fig. 2   Conventional RTL cryostat and photo-detector with components identified by labels. From reference 6.

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vacuum and electron beam for irradiation. Modifications were a variable temperature stage and a 2-position manipulator, both of which were designed and constructed locally. A sketch of the chamber is shown in Fig. 3, and photographs of the apparatus appear in Figs. 4 and 5. The detector was a Hamamatsu R1546 side view PMT; the high voltage supply and signal preamplifier were constructed locally. Detection was with a strip chart recorder. A heating and data acquisition system based on a Hyundai AT microcomputer, Techmar Labmaster AD/DA board, Barber Coleman temperature controller and commercial software was assembled. This was not fully implemented, however, as the SEM-RTL device was inoperable for extended periods of time, particularly near the end of the contract period (see below).

Operation of the unit is straightforward. The sample is placed in a copper curvette and covered with a stainless steel screen which serves to enhance heat transfer and minimizes charging during irradiation. The sample/curvette assembly is placed in the copper block sample holder, the stage inserted into the SEM and the system is evacuated. After suitable vacuum is achieved, the sample is cooled to 88 K (-185°C) by liquid nitrogen circulating through the sample holding block. With the manipulator in the retracted position indicated in Fig. 3, the sample is irradiated with electrons of predetermined energy for the time required to achieve the desired dose of 1 Mrad. This could be accomplished in 2 sec with a beam current of 10^{-7} amperes.
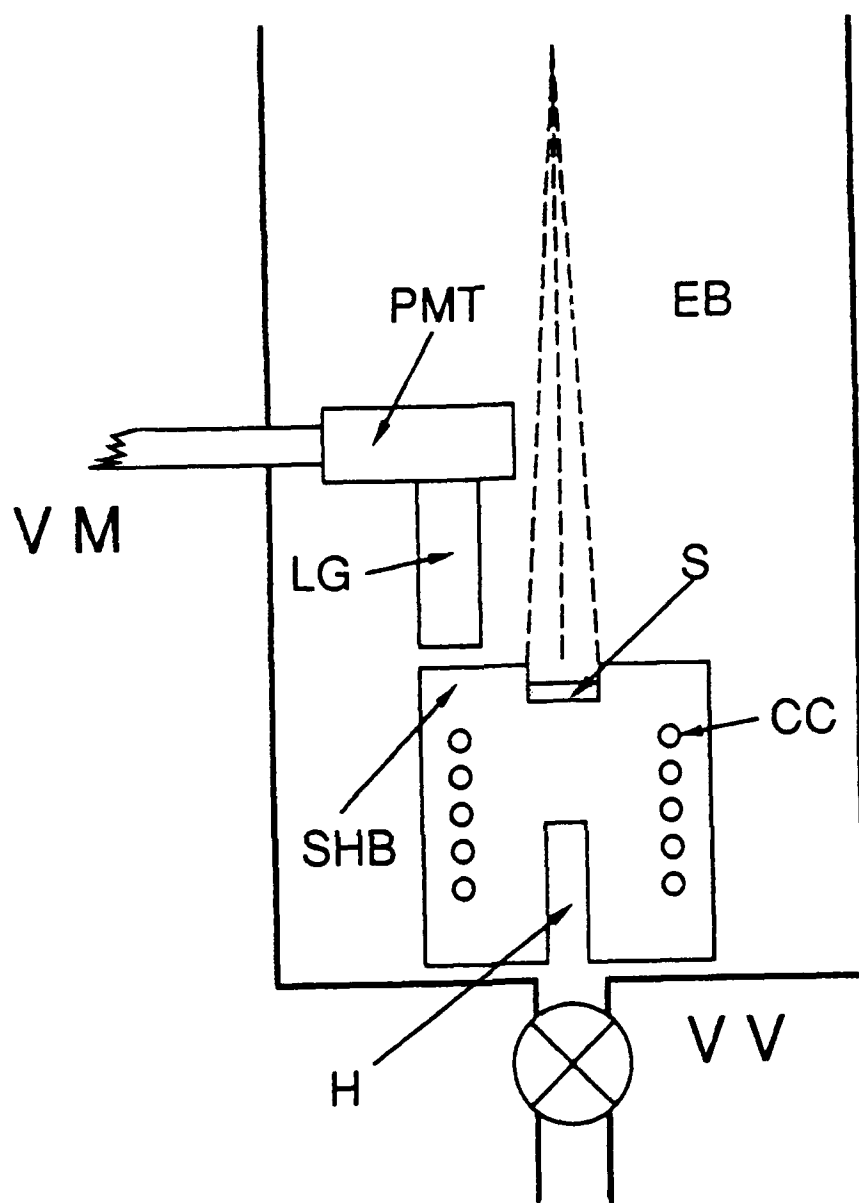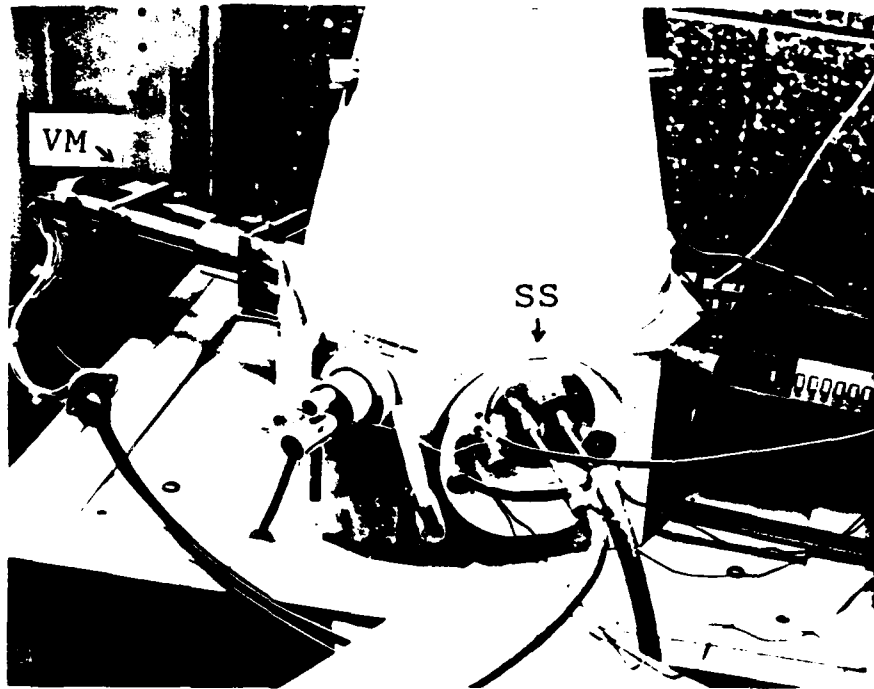
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Fig. 3   Schematic SEM-RTL device (not to scale). EB, defocussed electron beam; PMT, side-view photomultiplier tube; LG, light guide; VM, vacuum feedthrough manipulator for PMT position; SHB, sample holder block; S, sample in curvette; CC, cooling coils for liquid nitrogen; H, cartridge heater; VV, vacuum valve from SEM sample chamber.

Fig. 4   General view of modified Cambridge S4 SEM-RTL apparatus. Vacuum manipulator (VM) and specimen stage (SS) are identified.
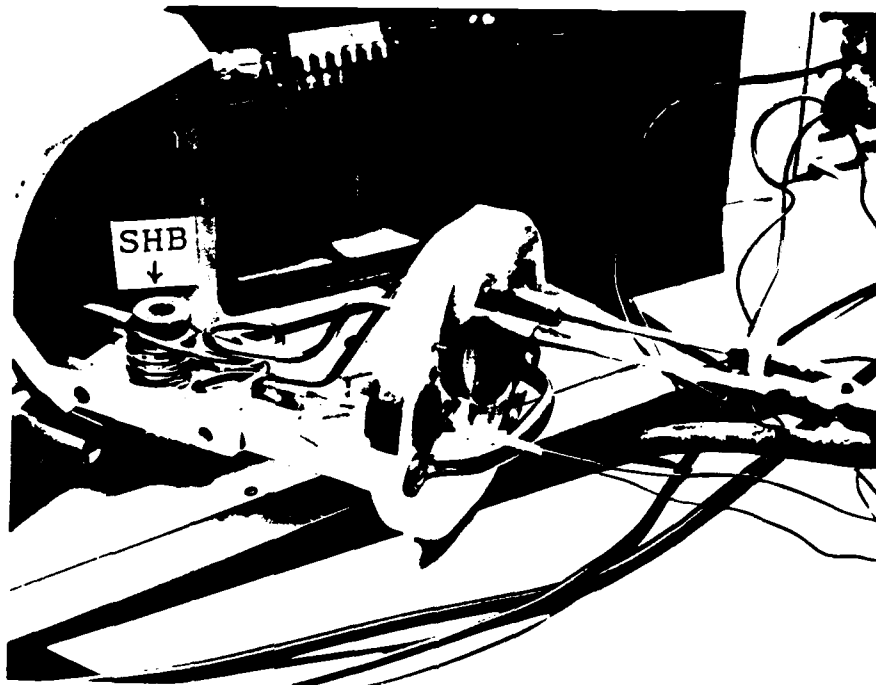
Fig. 5   View of specimen stage showing sample holder block (SHB).

Following irradiation, the still cold sample is viewed with the PMT by moving the manipulator. A light guide and heat shield (IR absorbing glass) were used to increase sensitivity and reduce spurious response at elevated temperatures. The temperature was increased at the selected rate β, and the RTL spectrum recorded.

B. SEM-RTL Performance

1. <u>Irradiation</u>. Medium energy (~10 keV) electrons have a penetration depth of a few μm, so the electron irradiation and subsequent RTL confined to these regions near the surface. Kanaya and Okayama[7] have derived an expression for the range R over which an electron penetrates before losing its initial energy E_o:

$$\rho R[\mu m] = 0.0276 \; E_o^{5/3}(A/Z^{8/9}) \qquad\qquad (8)$$

Here the sample density ρ is in g/cm^3, E_o is in keV, A is the atomic weight and Z the atomic number of atoms in the absorbing sample. Equation 8 gives R = 1.3 μm at 6 keV and R = 16.4 μm at 27 keV, the range of electron energies used in these experiments. This variation in irradiation depth permits in principle a type of depth profiling by RTL, though that was not pursued in this work.

Irradiation was done with a static beam defocussed to cover the curvette/sample surface (diameter of 1 cm). Beam current was measured at the sample position with a copper collecting plate connected to an electrometer. For calculating the radiation dose in rads (100 ergs/g), sample volume was area x R, where R is given

by eqn. 8.   With a beam current of 10^{-7} amperes, the target dose

of 1 Mrad could be achieved in a few seconds. Normally the current

was decreased and the radiation was done for 50-100 sec.

There was concern about charging effects influencing the

electron irradiation and subsequent RTL curve. The first SEM-RTL

experiments were done with samples coated with gold (100 Å thick)

to eliminate charging. It was found, however, that polymer films

in the curvette covered with a stainless steel fine mesh screen

behaved as if charging were unimportant. This was manifested by

reproducible RTL spectra which doubled in intensity as dose was

doubled, etc.

2.   **RTL Characteristics.**   Extensive testing was done to

compare SEM-RTL curves with those from "conventional" γ-irradiated

samples.   First, it was observed that the SEM-RTL sample gave

appreciable luminescence for about 10 minutes when held at 88 K

after irradiation. . This presumably happens during and after low

temperature γ-irradiation as well, but the interval of hours (or

days) between γ-irradiation and RTL enables this very low-temper-

ature phosphorescence to decay.

After a 10 minute wait to permit initial luminescence to

disappear, heating was started from 88 K at 10 K/min. Glow curves

obtained with the SEM-RTL generally resemble those from the

conventional unit at low temperatures, though differences are seen

at higher temperatures. Considering high density polyethylene as

an example (Fig. 6), an "extra" peak is seen with the SEM-RTL

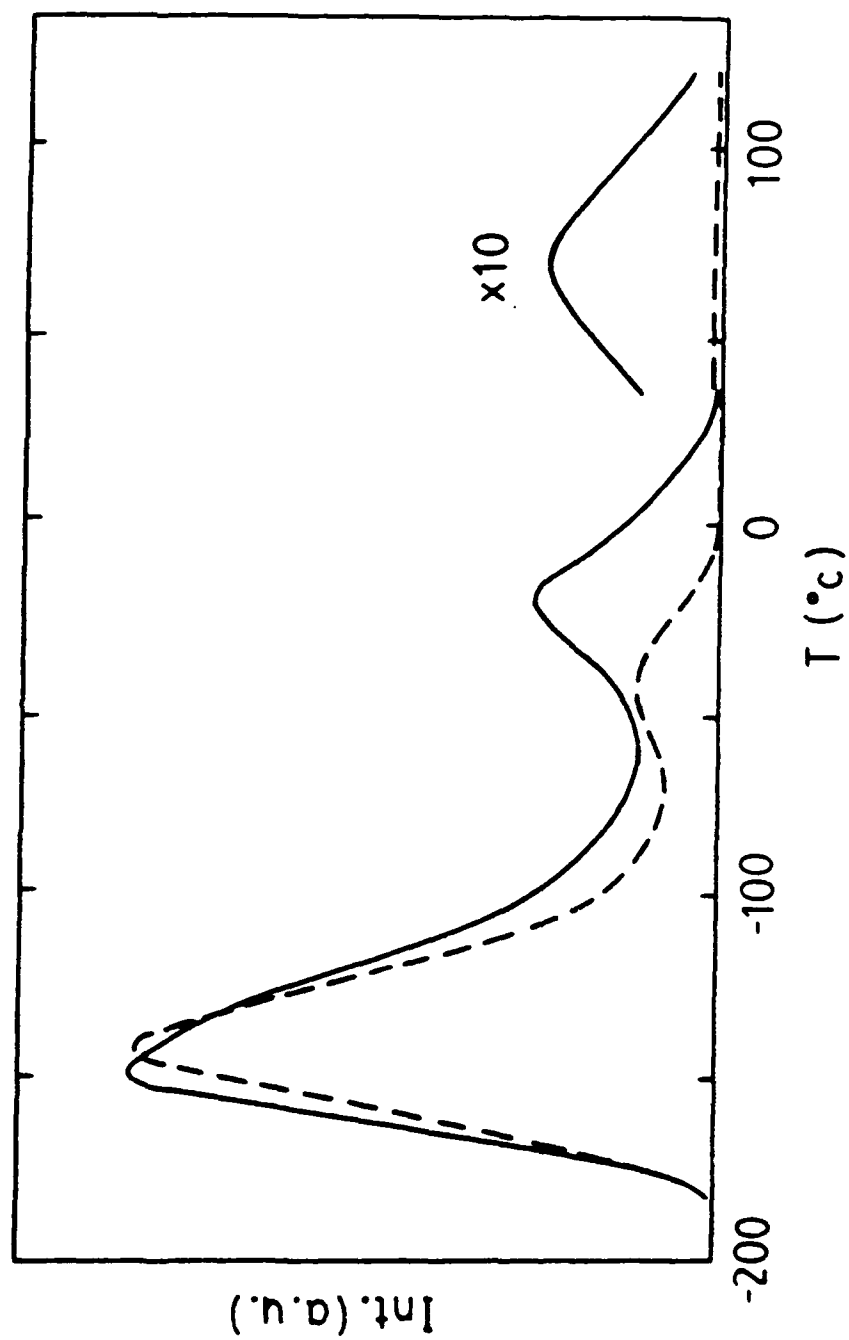experiment at 345 K (72°C); this high temperature peak is not seen

Fig. 6 RTL glow curves of high density polyethylene obtained with SEM-RTL (———) and conventional apparatus (----). Note enhanced intensity at elevated temperatures in the SEM-RTL curve.

with γ-irradiated polyethylene observed with conventional RTL apparatus. In the latter case, no RTL activity is present above 0°C. The difference is attributed to O_2 which is known to bleach RTL peaks, particularly those at higher temperatures.[3] The good vacuum in the SEM-RTL (P < 10^{-4} Torr) minimizes this O_2 effect. The conventional apparatus has no real control over the sample environment during heating, and the absence of high temperature peaks is an understandable artifact. The 345 K peak in linear polyethylene is the α relaxation process.[2]

The SEM-RTL was used to observe for the first time glow peaks associated with high temperature relaxations in nylon-6, poly(methyl methacrylate) and polystyrene at temperatures up to 418 K (145°C). These are discussed in more detail below.

3. <u>RTL</u>-<u>SEM</u> <u>Difficulties</u>. No fundamental problems were encountered. Considerable delays did arise, however, because of unreliable performance of the venerable Cambridge S4. The course of this research was frequently interrupted because of breakdowns, most frequently with the vacuum system. Repair was slowed because of limited availability of replacement parts. The SEM-RTL was totally unavailable for the final 8 months of the contract period due to blown transformers in the vacuum control circuitry. For this reason conventional RTL was used at the end of the project. It is unfortunate that high temperature RTL and environmental studies could not be pursued in the absence of the SEM-RTL apparatus.

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C.   RTL Studies of Polymers

A large number of polymers were examined by conventional RTL (γ-irradiation) and/or SEM-RTL (electron irradiation).

1.   __High Temperature Polymers__.   These were studied by conventional RTL (γ-irradiated to 1 Mrad at 77 K in vacuum). Figures 7 and 8 show results for different samples of polymides. The glow curve has four peaks (-135°C, -100°C, -30°C and +60°C), with considerable variation in relative intensities. These peaks are due to charge recombination, as heating unirradiated material from -180°C to +120°C gave no detectable luminescence. We note also that a +60°C peak is seen in this polymer, even though some O_2 is present when heating in the conventional RTL apparatus. In Kapton polymides (DuPont), the low temperature peaks are strongly suppressed relative to the +60° peak in the thin film. Generally similar behavior is seen in the two Dow 2080 polymides (Fig. 8), though these samples have the same thickness and are (a) solvent cast and (b) heated to 280°C. On this basis it is conjectured that the imidization reaction is not so complete in the thick Kapton film in Fig. 7.

Similar peaks at -100°C, -30°C and +60°C were seen in a polyamideimide (Torlon from Amoco), though the intensity was very low. A polyetherimide (Ultem from General Electronic) displayed only one peak at -30°C.

RTL spectra from a polyethersulphone (Stablar S100 from ICI Americas) and a polyetheretherketone (Stablar K200 from ICI Americas) were similar to one another, having a strong maximum at
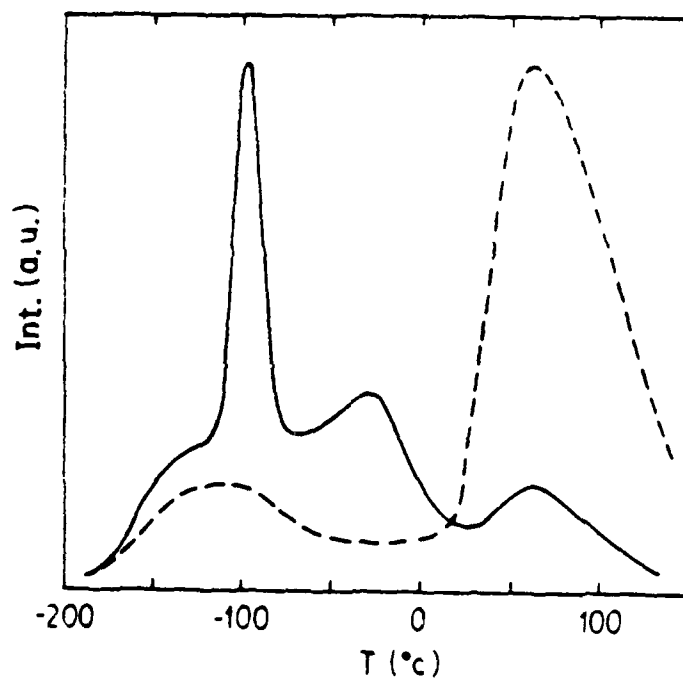
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Fig. 7   RTL glow curves of DuPont Kapton polymide films of thickness 125 μm (——) and 8 μm (----). Conventional RTL, γ-irradiation.
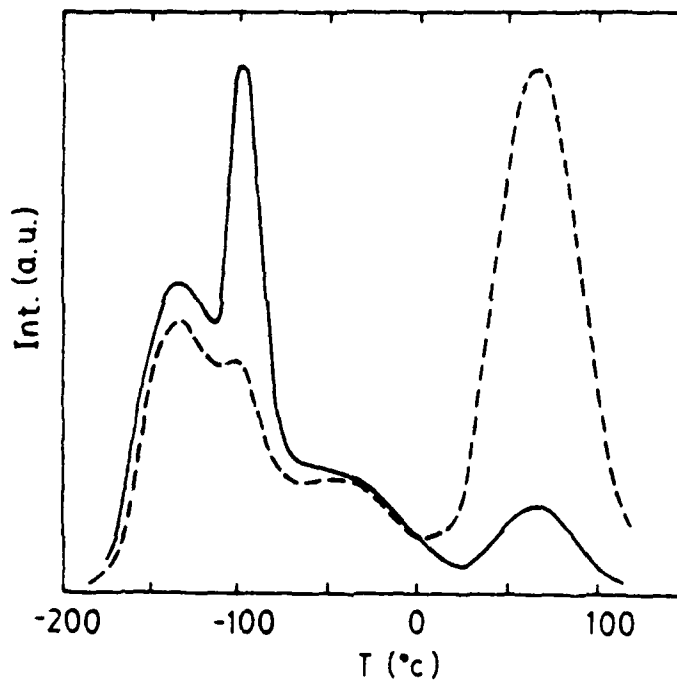

Fig. 8   RTL glow curves of Dow 2080 polymides as cast from dimethyl sulfoxide (——) and after heating to 280°C (----). Conventional RTL, γ-irradiation.

-130°C followed by a continuously decaying glow up to 120°C, the maximum temperature investigated.

In general terms, the observation of relatively intense maxima at +60°C is consistent with the stiffness and thermal stability of those polymers. No attempt has been made to relate these RTL peaks with relaxation processes as transitions seen by other methods.

2. <u>Poly(ethylene oxide)</u> was examined by conventional RTL (γ-irradiation, 1 Mrad at 77 K in vacuum) as a function of doping with NaSCN. Addition of salts leads to ionic conductivity, and also affects the dynamics of polymer chains in which the salt is dissolved.[8] The most conspicuous feature is the broad intense peak at -130°C (Fig. 9) which appears to shift to -145° when a mole fraction x = 0.125 of NaSCN is added. The presence of salt also generates a shoulder at -110°C and significantly increases the peak near -60°C.

These peaks at -60°C and -110°C correspond to locations of ß and γ relaxations seen by dielectric and mechanical loss.[2] One notes, however, that the low temperature γ peak by RTL is much more intense than the -60°C (glass transition) peak, while just the opposite is true by other methods (see reference 2, pp. 551-561). This is another example of the unique sensitivity of RTL, i.e., the ability to emphasize the visibility and apparent importance of certain relaxation processes which are difficult or impossible to observe by other methods. In the present instance of poly(ethylene oxide), mechanical and dielectric loss generally agree with one
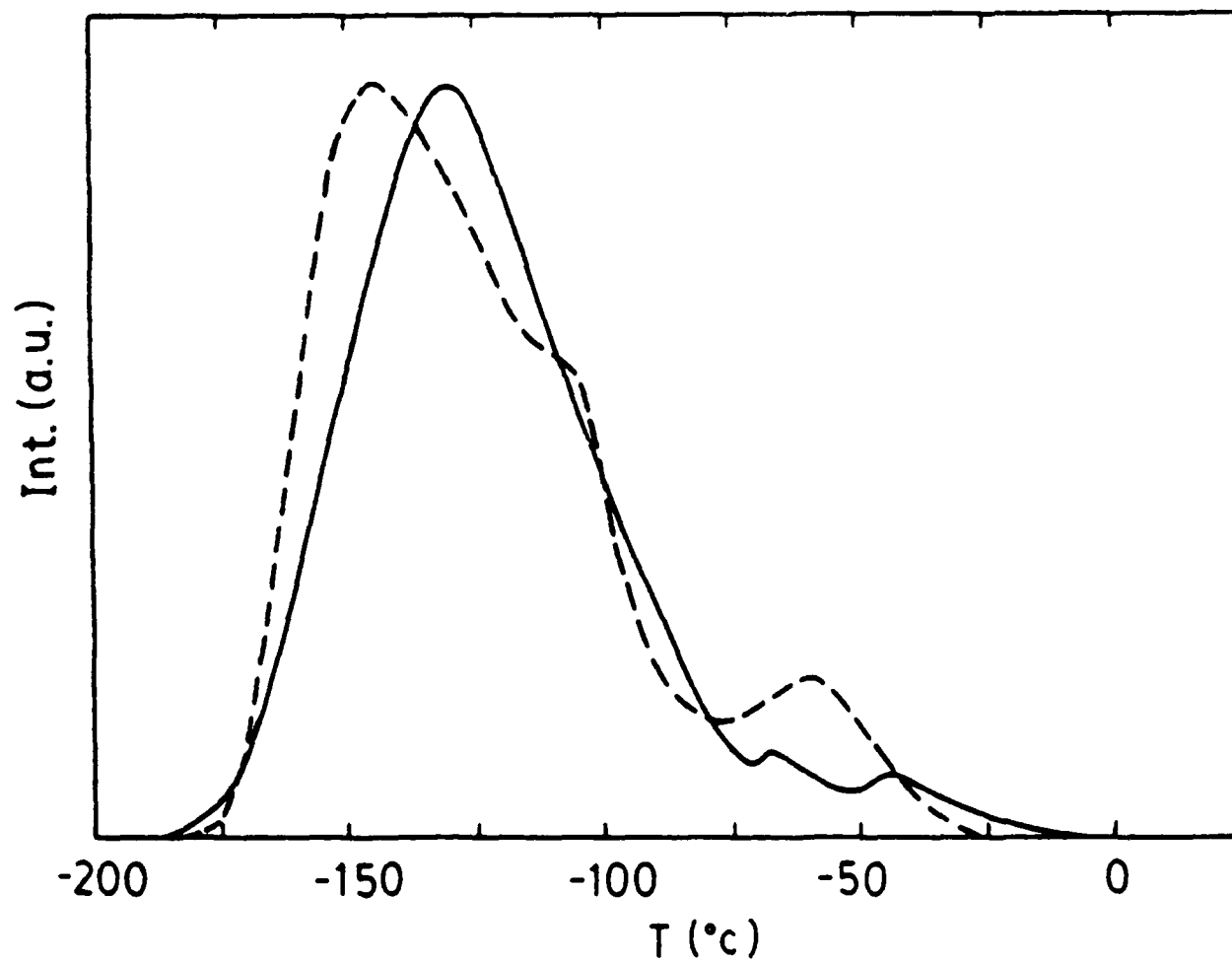
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Fig. 9   RTL glow curves of poly(ethylene oxide) (——)
and poly(ethylene oxide) with 12.5 mole % NaSCN
(----).   Conventional RTL, γ-irradiation.

another,[2] while the intensity distribution by RTL is fundamentally different. It is not known which pattern of relative intensities is correct, though it is quite possible that the higher temperature β process (-60°C) is suppressed in RTL by some of the bleaching mechanisms described below.

3. High Temperature SEM-RTL. The issue of RTL at high temperature is fraught with uncertainties. Luminescence can be by either fluorescence or phosphorescence, and the latter is subject to thermal bleaching.[4] By this one means that long lived excited states represented by L* in eqn. 3b,c can be deactivated by collisions if sufficient thermal energy is available. Such radiationless transitions to the ground state will decrease α in eqn. 5, thus diminishing the intensity of a glow peak. Added to this is the quenching effect of molecular oxygen which is frequently present. Oxygen quenching of RTL has been studied most thoroughly for polyethylene, as reviewed in Chapter 3 of reference 3. While no claim to mechanistic understanding is asserted, it is clear that higher temperature peaks are more efficiently quenched, probably because of the enhanced mobility of O_2 quenchers at increased T.

The vast majority of RTL results presented to date deal with low temperature relaxations or transitions, i.e., those in the range of temperatures between 77 K and 273 K (-193°C and 0°C). The low pressure environment of the SEM-RTL apparatus certainly minimizes any effect of oxygen quenching. Furthermore, restriction

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of the observed volume to a surface region about 10μm thick means that dissolved oxygen in the effective sample is greatly reduced by outgassing during initial evacuation of the sample chamber at temperature.

With this in mind, a number of polymers were examined for RTL above 0°C. One example (linear polyethylene, Fig. 6) has already been given; here a weak glow peak was seen at 72°C (344 K). Nylon 6, similarly examined by SEM-RTL after electron irradiation at 88 K, showed a peak at 80°C which is probably from the glass transition in this semicrystalline polymer. High temperature peaks were also seen at 50°C and 148°C in poly(methyl methacrylate) and at 60°C and 120°C in polystyrene. These nearly correspond to the temperature locations of "beta" secondary relaxations and glass transitions, respectively.[2] The transitions seen here are true RTL phenomena, as no activity was seen over the same temperature range with unirradiated samples. There is no report of these RTL peaks in either nylon 6 or poly(methyl methacrylate). One study has been made of polystyrene which gave peaks at -97°C, -52°C and +105°C.[9] While the latter is certainly in a position appropriate for T_g in polystyrene, the two low temperature peaks in that work have never been seen by RTL[3] or by other methods.

In concluding this section it should be mentioned that very sharp RTL peaks associated with crystal-crystal phase transformations in n-paraffins[10] and crystal melting in poly(oxymethylene)[11] and extended chain crystals of polyethylene[12] have been observed above 0°C. These first-order thermodynamic transitions do not

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conform, of course to eqn. 5, and the RTL peaks are very narrow (1°C). Since the solubility of O_2 in polymer crystals is low, it is reasonable that O_2 quenching is not effective in these transitions. Melting transitions were not looked for in this study.

D.   Quantitative Aspects of RTL.

1.   Relative Shapes of Glow Curves. It is well established that chemically quite similar polymers have remarkably different properties. They also have quite different RTL spectra as shown for high and low density polyethylenes in Fig. 10 (SEM-RTL). It should be emphasized that there are no clear "assignments" for the peaks in these spectra. A major reason for this confusion is very simple - uncertainty in comparison of RTL intensities from sample to sample. In Fig. 10 we have "normalized" the most intense peaks (-140° K for HDPE, -25°C for LDPE) to unity for convenience. Proper comparison of RTL intensities requires (1) reproducibility within one material and (2) knowledge of and control over those parameters controlling the intensity.

Numerous experiments were done to verify reproducibility with one material (γ-irradiation, conventional RTL). In accord with previous studies, intensity was linear with irradiation dose over the range considered (0.1 - 1 Mrad). Intensity was also proportional to sample size under most conditions. (This would not pertain to electron irradiated SEM-RTL samples of thickness greater than the penetration range of the electrons). A series of model copolymers of ethylene and butene-1 were used to assess absolute intensities. Those had been synthesized locally, so impurity
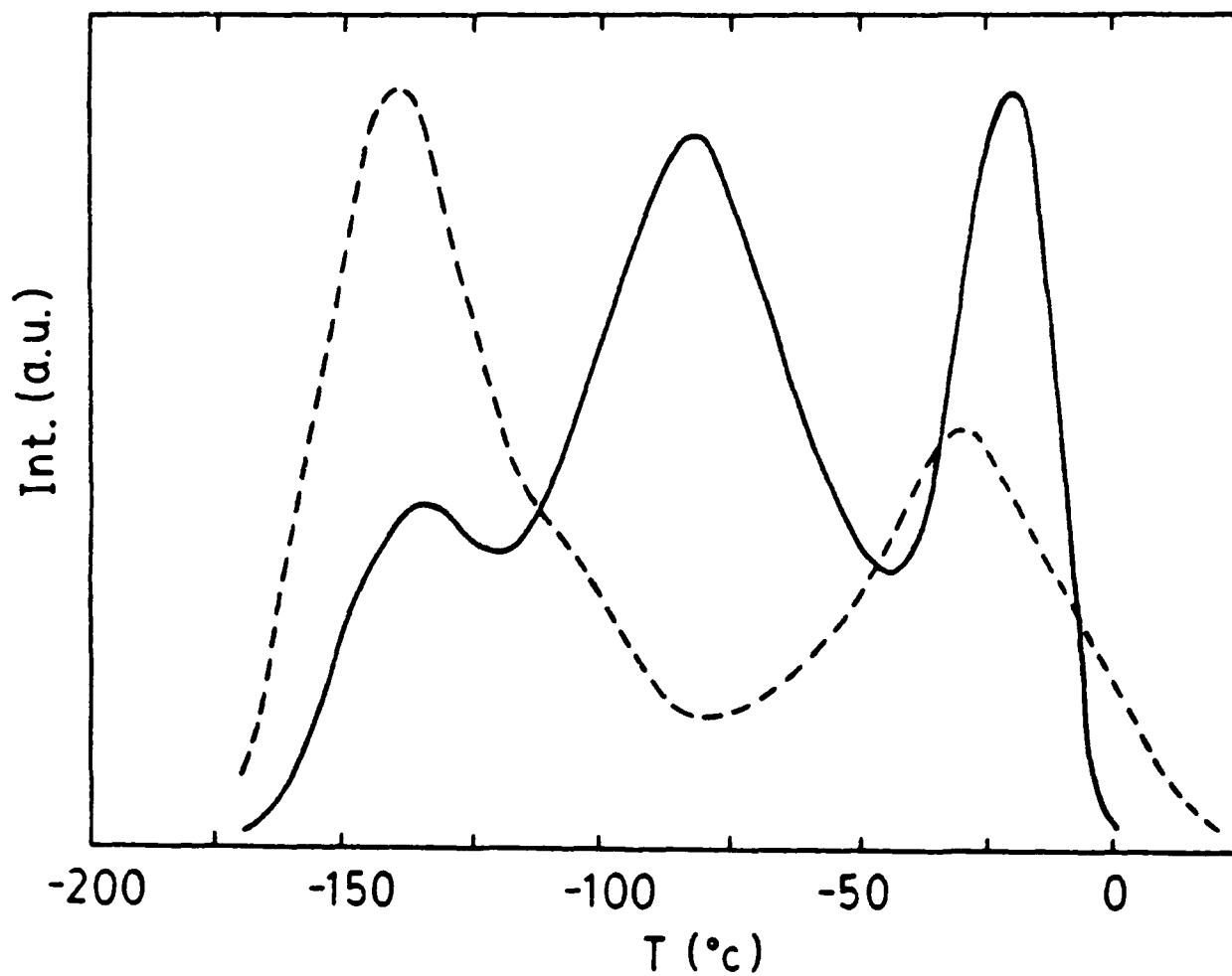
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Fig. 10 RTL glow curves of low density polyethylene
(——) and high density polyethylene (----).
Intensities are arbitrarily adjusted so largest
peak heights are equal.

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contents should be as "constant" as possible. These copolymers varied in short chain branching from 20 to 100 per 1000 backbone carbon atoms, and in room temperature crystallinity from 40% to 0%. Different size samples of those polymers were investigated by conventional RTL. The results were quite unexpected. First, the relative peak intensities did not change (even though morphology and properties certainly did). Even more disquieting was the observation that absolute RTL intensity, normalized for sample size, varied by a factor of 4 with no discernible pattern.

From this it must be concluded that relative spectrum shapes, but not "absolute" intensities, are available from RTL. Intensity (even given the most careful radiation and handling protocols, etc.) ultimately depends on the presence luminescent impurities (eqn. 3b and 3c) over which the experimenter has little or no control. Furthermore, the detected light emission obviously depends on the optical transmission characteristics of the sample. Light scattering effects in particular are known to change with morphology and composition in multiphase systems. We suspect that optical properties would be less important in SEM-RTL than with γ-irradiated samples, as the luminescence in the former case comes from near surface regions.

2. <u>Widths of Transition Peaks</u>. One feature of RTL "spectra" is the narrowness of the peaks when compared to those from mechanical or dielectric loss experiments. In practical terms this is an advantage, as "overlapping" processes can be resolved and apparent transition temperatures located with greater certainty.

Notice in Fig. 10 that the full width at half-maximum height of the peaks is about 15-20°C. Other narrow and broad peaks are seen in other data in the report. An excellent example of the narrowness of the RTL "transition" is provided by the work of Zlatkevich and Nikolskii[13] for a random copolymer of styrene (30%) and butadiene (70%). Here the width $\Delta T = 5°$ for the RTL peak, and about 50° for the mechanical loss peak.

Simple model calculations were done to clarify this difference. Equation 5 was used to calculate model peak profiles with different kinetic parameters. A frequency factor $\omega = 10^{12}$ sec^{-1} was assumed, together with a single (temperature dependent) relaxation time governed by Arrhenius (eqn. 1a) or WLF (eqn. 1b) laws. The results in Fig. 11a are for Arrhenius activation; notice that the width of an elementary peak increases from about 10° to 30° for peak temperatures T_p from 170 K (-100°C) to 340 K (60°C). For the glass transition the universal WLF constants[1] were employed; Fig. 11b shows that $\Delta T \approx 3°$. Increasing the heating rate β by a factor of 10 shifts T_p upward by 3°, leaving the width sensibly unaffected. Virtually identical peaks are calculated for the mechanical loss factor tan δ with equivalent single relaxation time models.

It is unlikely in the extreme that the narrow RTL peaks truly reflect the range of mobilities in a polymer around any particular relaxation or transition. Experimental RTL peak widths are comparable to theoretical ones calculated with a single relaxation time (no distribution of relaxation times). One plausible
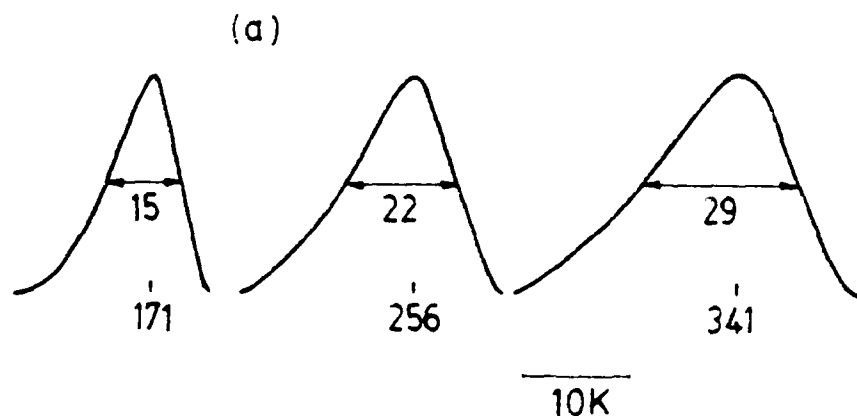
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(a)

Fig.11(a) RTL curves calculated from eqn. 5 with ω = 10^{12}sec^{-1} and E_a = 10 kcal/mole (left) E_a = 15 kcal/mole (center), E_a = 20 kcal/mole (right). Full width at half maximum (K) is indicated for each peak.
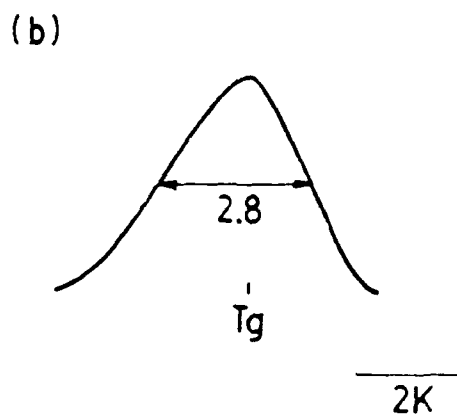
(b)

Fig.11(b) RTL curve calculated by a variant of eqn. 5 to simulate the peak arising from a glass transition (eqn. 1b).

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explanation is that RTL peaks are narrowed on the high temperature side by some sort of quenching process. It is conceivable that, once the polymer matrix starts moving in response to thermal activation, the resultant luminescence photobleaches[3] those charges which have yet to recombine. In a similar fashion, the added mobility could lead to thermal bleaching of the high temperature portion of a distributed relaxation process. But this does not explain the fact that the RTL process does not seem to start for many 10's of degrees after the onset of mechanical loss. At this time the narrowness of RTL peaks must be accepted as an empirical fact.

III. CONCLUSIONS

Radiothermoluminescence from polymers irradiated with medium energy (5-30 keV) electrons is shown to be a very good method of performing RTL for the study of molecular motions and relaxations. The environmental control (high vacuum) needed for electron irradiation eliminates the suppression of peaks by oxygen bleaching. Experiments with the SEM-RTL apparatus are fast (about 30 min) and convenient. The only fundamental limitation is that only the near surface regions (depth of 1-10 μm) are examined by this method. This should be considered if the characteristics of the surface differ appreciably from those in the bulk.

With the O_2-free environment of the SEM-RTL, high temperature relaxations were observed in various thermoplastics at temperatures as high as 150°C (423 K). Aside from this, the electron based SEM-RTL gives the same results as conventional RTL employing γ-irradiation.

Consideration of absolute RTL intensities showed that these are reproducible in a single polymer material but vary erratically from one polymer to another. Without any method to compare RTL intensities, meaningful comparisons of different RTL spectra are not achievable. It also appears that the RTL "peaks" are unphysically narrow, i.e., they do not represent the range of mobilities which are present in polymer solids.

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V. APPENDIX

A. Personnel Supported

      Lev Zlatkevich, Research Associate (full time).

      Buckley Crist, Jr., Professor, (part AY, summer).

B. Papers Presented

      "Radiothermoluminescence of Polymers with a Modified Scanning Electron Microscope", L. Zlatkevich and B. Crist, Federation of Analytical and Spectroscopy societies, 13th annual Meeting, St. Louis, MO, Oct. 1, 1986.

      "Radiothermoluminescence in Polymers", L. Yu Zlatkevich and B. Crist, American Physical Society March Meeting, New Orleans, March 23, 1988. [Bulletin Amer. Phys. Soc. 33(3), 506 (1988)]

C. Paper Written

      "Radiothermoluminescence with _in situ_ Electron Irradiation", B. Crist, submitted to J. Polym. Sci:; Part B; Polym. Phys.